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BRIEF COURSE IN  
METALLURGICAL ANALYSIS

BY

HENRY ZIEGEL

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## **METALLURGICAL ANALYSIS.**

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BRIEF COURSE IN

# Metallurgical Analysis

BY

Henry Ziegel

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TO PROFESSOR G. P. BAXTER,  
Teacher, Investigator, Friend

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# INTRODUCTION.

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This book is written for the use of upperclassmen, trained in elementary qualitative and quantitative analysis. The work outlined in the procedures should require one-fourth to one-fifth the students time, some ten to twelve hours a week—during two successive semesters. Since few calculations are implied, the student should have or have had accompanying his previous course, a series of problems in chemical arithmetic.

The author's object then, has not been to describe all the methods for determining the composition of metallurgical products, rocks and ores, but to describe a series of standard analyses in daily use in various analytical laboratories. The procedures have been so chosen so as to avoid the same determinations as much as possible. Procedures for similar substances have been mentioned in the notes or referred to in the bibliography. Since such a selection is always open to comment, the author welcomes criticism and suggestion.

The analyses of gases, fuels and water, form a sub-division which may well be treated in a separate course; but several articles on sampling<sup>1</sup> should be read by the student.

By binding the laboratory sheets with the notes, neatness and original data are continually suggested to the student.

Finally, due credit must be given to the authors of the larger works on the subject, *viz.*:

Blair: "The Chemical Analysis of Iron." 7th ed.

Johnson: "The Chemical Analysis of Special Steels." 2nd ed.

Low: "Technical Methods of Ore Analysis."

Lord and Demorest: "Metallurgical Analysis."

Price and Meade: "Technical Analysis of Brass."

Smith: "Electro-Analysis" 5th ed.

Classen: "Quantitative Analysis by Electrolysis," Tr. Hall.

Betts: "Lead Refining by Electrolysis."

"Methods of Analysis of Carbon Free Metals," Monograph by Goldschmidt Co.

"Treadwell," 3rd ed., and "Fresenius," 6th ed., on the entire subject of analysis.

The Journals and Abstracts of The American Chemical Society.

The publications of the American Electrochemical Society.

The publications of the Bureau of Standards, Washington.

The publications of the Bureau of Mines, Canada.

The reader's attention is called to the procedures and notes on the analyses including the use of the hydrogen and calomel electrode<sup>2</sup> (work of Sand, Schoch, Hillebrand and Forbes and Bartlett). To be sure these procedures require special equipment and some skill, yet the results obtained with them are so satisfactory and lead to such interesting future application that the student should study these procedures in detail.

# IRON ORES, IRON AND STEEL, CHIEF CONSTITUENTS.

## SILICA IN ORES.\*

There are two general methods for the determination of silica in ores; by solution and by fusion. Several general details of manipulation are emphasized once for all in the first few procedures.

**Procedure No. 1.**—Dissolve 1 gram of ore in 15 cubic centimeters HCl specific gravity 1.2 in a small beaker provided with a cover glass; warming until the ore is decomposed. Oxidize any ferrous iron with a few drops of  $\text{HNO}_3$ , continue heating, wash off the cover glass, and evaporate until the solution is quite syrupy. Evaporate to dryness and bake at  $110^\circ \text{C}$ . for 15 minutes. Cool, redissolve in HCl, evaporate and rebake. Redissolve in 30 cubic centimeters HCl 1-3, and filter through a small ashless paper using a policeman of  $\frac{1}{8}$ -inch glass rodding tipped by a small piece of well washed rubber tubing. It is well to remember that many applications of small quantities of water will wash out more precipitate than few applications of less small quantities.

Wash the filter paper free from iron by using warm wash water containing a little HCl (5 to 10 cubic centimeters per liter), remove paper from funnel with tip of finger nail or drawn out end of a policeman, and place in a weighed 20-gram platinum crucible. Char, ignite, cool and weigh. Add two drops  $\text{H}_2\text{SO}_4$  specific gravity 1.84, and 7 cubic centimeters  $\text{H}_2\text{F}_2$ . Ignite over a ring burner,\* cool and reweigh. Difference between weighings is  $\text{SiO}_2$ . Wait at least 30 minutes after putting crucible into desiccator before removing to weigh.

**Procedure No. 1, part 2.**—Place 1 gram of ore with 7 to 8 grams sodium carbonate in a 30-gram platinum crucible, stir the mixture thoroughly with a thin glass rod, wipe off latter with a piece of filter paper, and add the paper to the charge. Heat to quiet fusion, chill the crucible in water, and dissolve

---

\* The cylinder described by Hildebrand, Bull. U. S. G. S., No. 422, p. 31, may be used instead.

the melt in 40 cubic centimeters HCl 1-3. Remove the crucible and cover from the HCl solution with a glass rod, add a few drops HNO<sub>3</sub>, and proceed as above, oxidizing with HNO<sub>3</sub> ff.

### SILICON IN IRON AND STEEL.

**Procedure No. 2.**—Dissolve from 2 to 5 grams of steel in 20-40 cubic centimeters nitric acid 1-1 in a platinum dish covered with a cover glass, wash off cover glass into dish and evaporate contents to dryness on the air bath. Increase the heat to decompose ferric nitrate, and bake for ten minutes. Redissolve in 10 cubic centimeters concentrated HCl slowly and again evaporate to dryness and bake. Redissolve in HCl and add 100 cubic centimeters water, decant, filter and purify as before. Factor  $\frac{1}{5}$  of 0.4693 for 5 grams.

Or silicic acid in dilute acid solution may be completely dehydrated by 20 cubic centimeters of H<sub>2</sub>SO<sub>4</sub> 1-1 upon boiling to fumes of SO<sub>3</sub>, cooling and diluting. Filter hot and determine the silica as before.

Twenty-five cubic centimeters of the following solvent may be added all at once. Water, 50 cubic centimeters; concentrated H<sub>2</sub>SO<sub>4</sub>, 40 cubic centimeters; concentrated HNO<sub>3</sub>, 80 cubic centimeters; concentrated HCl, 60 cubic centimeters. Ferro silicons require fusion with Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>O<sub>2</sub>, preferably in a nickel crucible.

Silica in slag is determined by moistening 5 grams in a casserole with a few drops of water stirring in 5 cubic centimeters HCl and warming until the slag gelatinizes. Two evaporations from HCl solution are followed by the usual fusion and purification.

### PHOSPHORUS.

Phosphorus is determined as the yellow precipitate, (NH<sub>4</sub>)<sub>3</sub> PO<sub>4</sub> · 12MO<sub>3</sub>, containing 1.63 per cent. P. The precipitate may be weighed as such, or dissolved in a pipetteful of standardized NaOH, and the excess alkali titrated with standard HNO<sub>3</sub>, using phenolphthalein as an indicator.

The following conditions must be observed for quantitative precipitation.

Absence of HCl and of organic matter.

Presence of ammonia as nitrate or sulphate.

**Sample No.**

[illegible]



Presence of 30-60 molecules of sulphuric or better nitric acid per molecule  $P_2O_5$ .

Phosphorus should all be present as tribasic phosphoric acid.

Temperature should never exceed  $80^{\circ} C.$ , and should be around  $40^{\circ} C.$  (At elevated temperatures  $MO_3$ , which cannot be removed, will precipitate, so also may compounds of iron and ammonia with  $MO_3$ .) A convenient procedure is to neutralize the paste of  $Fe(OH)_3$  with dilute nitric acid, and after adding the precipitating solution, merely set aside to cool and coagulate for about an hour.

**Procedure For Iron Ores, No. 3.**—Weigh 2, 1.63, or a multiple grams of ore into  $\frac{1}{4}$ -liter Erlenmeyer flask and dissolve in 15-40 cubic centimeters concentrated  $HCl$ . Filter and wash; ignite residue. Fuse latter with 2 or 3 grams  $Na_2CO_3$ , dissolve fusion in  $HCl$ , evaporate both solutions down to dryness and bake, preferably repeating. Cool, dissolve in as little  $HCl$  as possible, combine the two solutions and filter off  $SiO_2$ .

To the filtrate in an Erlenmeyer flask add 30 cubic centimeters concentrated  $HNO_3$  free from yellow fumes and evaporate to syrupy; repeat so as to rid of last traces of  $HCl$ .

(Iron and steel should be dissolved in dilute  $HNO_3$ , the silica dehydrated (as Procedure No. 1); the resulting solution in  $HCl$  treated with  $HNO_3$ , and the following common procedure followed.)

Add  $NH_4OH$  to filtrate in an Erlenmeyer flask to form a thick paste, and dissolve this paste in  $HNO_3$  1-1, giving somewhat less than 200 cubic centimeters of amber colored solution at about the proper temperature to add 60 cubic centimeters of the precipitant.\* Shake the solution for five minutes, remove stopper and let stand for 1 hour. Filter into a weighed gooch crucible, wash precipitate thoroughly with 10 per cent.  $NH_4NO_3$  solution, twice with water and twice with alcohol, dry for 40 minutes at  $110^{\circ} C.$ , cool and weigh.

\* Molybdate solution. Dissolve 10 grams of molybdic anhydrid in 50 cubic centimeters  $H_2O$  containing 8 cubic centimeters  $NH_4OH$ . Filter through asbestos and pour it into a mixture of 40 cubic centimeters  $HNO_3$  and 60 cubic centimeters  $H_2O$ . Stir while mixing, and keep cool, add one drop of microcosmic salt solution, and let settle for 24 hours before decanting for use.

## Analysis of

**Sample No.**

[illegible]

Instead of weighing the yellow precipitate it may be dissolved in a pipette full of NaOH and the excess NaOH titrated with  $\text{HNO}_3$  using 1 drop of a 1 per cent. alcoholic solution of phenolphthalein as an indicator. In this case, an ore or a steel of known phosphorus content should be run at the same time, so as to determine the phosphorus equivalent of the standard acid and alkali.

Standard  $\text{HNO}_3$ , 20 cubic centimeters concentrated  $\text{HNO}_3$  per liter of water.

Standard NaOH, saturate 30 cubic centimeters  $\text{H}_2\text{O}$  with NaOH and use upper  $\frac{2}{3}$  in a liter of water. These solutions should be made equivalent.

The yellow precipitate may be titrated with permanganate by the Emmerton method involving solution in ammonium hydroxide, reduction of the acidified with  $\text{H}_2\text{SO}_4$  solution in a Jones reductor and oxidation of the reduced molybdenum compound by ordinary  $\text{KMnO}_4$  solution. This is much used, but offers no decided advantages over the methods given above.

For the analysis of special steels, Johnson or Demorest should be consulted.

### SULFUR.

The sulfur assay generally involves the oxidation of S to  $\text{SO}_2$ , and the subsequent precipitation of  $-\text{SO}_4$  by  $\text{Ba}^{++}$ . As some  $\text{SO}_2$  is evolved by the combustion of ordinary illuminating gas, it is advisable to use only alcohol or gasoline flames when determining sulfur. The crucible may, however, be placed in a large square of asbestos board which has been punched to receive it; and the regular Bunsen used.

It is advisable to pour the barium solution into the sulfate solution as less soluble barium salts will thus contaminate the precipitate. Even if this is carried out,  $\text{BaSO}_4$  will include (enclose) and occlude (attract and stick to)  $\text{BaCl}_2$ , alkali chlorids and  $(\text{NH}_4)_2\text{SO}_4$  appreciably if there is much  $\text{BaSO}_4$  formed. Hence it is advisable to have as little precipitate as accuracy will permit.

$(\text{NH}_4)_2\text{SO}_4$  will be lost on ignition, but occluded as well as included  $\text{BaCl}_2$  will make the precipitate heavier. Occluded nitrates may cause high results. High iron concentrations especially if present as  $\text{Fe}^{\text{III}}$  will cause high results unless considerable HCl is present, on the other hand  $\text{BaSO}_4$  is slightly soluble in excess HCl. Too high temperature during ignition will give BaO.

The precipitate of  $\text{BaSO}_4$  comes down so fine that digestion on the steam bath for an hour is advisable to prevent the precipitate from running through the filter. Or, the precipitate may be allowed to settle over night at room temperature.

## Analysis of

**Sample No.**

[illegible]

**Procedure For Iron Ores, No. 4.**—Mix 1 gram of ore with about 5 grams  $\text{Na}_2\text{CO}_3$  and 0.5-1 gram  $\text{NaNO}_3$  in a 30-gram platinum crucible by stirring and adding the filter paper wipings to the crucible. Heat to quiet fusion, remove from heat and chill the outside of the crucible by dipping in water. The contents are then removed into a beaker containing about 75 cubic centimeters warm water and the crucible and cover washed out into and removed from the beaker. The melt is dissolved by heating; dilute  $\text{HCl}$  is added carefully until the effervescence ceases, a few drops of alcohol added to precipitate  $\text{Mn}$ , and the solution is filtered. To the filtrate is added 25 cubic centimeters of a 5 per cent. solution of  $\text{BaCl}_2$ , or better pour the hot solution into 25 cubic centimeters of a 5 per cent.  $\text{BaCl}_2$  solution diluted to 100 cubic centimeters. After digesting on a steam bath or allowing to settle over night, the supernatant liquid is decanted through the filter, and the  $\text{BaSO}_4$  is filtered off and weighed. It is advisable to dry the precipitate, separate it from the filter onto glazed paper and ignite the filter separately by winding around it a piece of platinum wire the end of which is sealed into a piece of glass tubing: holding the burning paper above the weighed crucible. The bulk of the precipitate is then brushed from the glazed paper into the crucible, and the latter ignited, cooled and weighed. It is also advisable to give the crucible an  $\text{H}_2\text{F}_2$  treatment (adding two drops of concentrated  $\text{H}_2\text{SO}_4$ ) to rid of silica. (Since iron ores are apt to be very low in S, 2-5 grams of sample may be taken.)

The oxidation of sulfur in iron and steel is accomplished by not too rapid solution of 2-5 grams in 25-40 cubic centimeters concentrated  $\text{HNO}_3$  in a platinum dish with subsequent addition of a few cubic centimeters of concentrated  $\text{HCl}$  and 0.5 gram  $\text{KClO}_3$ . Evaporate to dryness, bake, dissolve in  $\text{HCl}$  and rebake. The  $\text{Na}_2\text{SO}_4$  may then be washed out of the  $\text{Fe}_2\text{O}_3$  by warm water, and the solution of  $\text{Na}_2\text{SO}_4$  poured into 5 per cent.  $\text{BaCl}_2$  solution as above. Or the  $\text{Fe}_2\text{O}_3$  may be dissolved in  $\text{HCl}$  and the  $\text{BaCl}_2$  solution added to this. In this latter case, it is advisable to reduce the iron to the ferrous condition by  $\text{Al}$  powder before precipitation of  $\text{BaSO}_4$  as less contamination of the precipitate thus results.

## Analysis of

**Sample No.**

[illegible]

Sulphur in 1.3736 grams pyrites ore may be oxidized by 10 cubic centimeters of a mixture of 2 parts by volume liquid Br and 3 parts  $\text{CCl}_4$  in the cold. For mattes, concentrated  $\text{HNO}_3$  saturated with  $\text{KClO}_3$  may be used. The subsequent procedure is the same as in the case of iron and steel.

Sulfur may be determined volumetrically by evolution as  $\text{H}_2\text{S}$  which is absorbed in ammoniacal  $\text{CdBr}_2$  solution. This is rendered acid with  $\text{HCl}$  and the  $\text{H}_2\text{S}$  changed to  $\text{HI}$  with iodine solution which has been standardized against bichromate solution of known strength. The end point is the blue color imparted to starch solution by free iodine.

### CARBON.

The direct combustion method, using an electric furnace and an oxygen tank fitted with a diaphragm valve, is the method most often used for the determination of carbon in steel and iron. It is often superseded by metallographic methods.

Oxygen is purified by passing through  $\text{KOH}$  followed by  $\text{H}_2\text{SO}_4$ ,  $\text{Zn}$  and  $\text{CaCl}_2$  bottles and tubes in the order named. It then passes through a  $\frac{7}{8}$ -inch silica combustion tube set in the furnace. The sample is placed in a groove made in a sand or alundum lining of a boat of platinum, silica, alundum or porcelain. The boat is put into the furnace through the end nearer the oxygen tank. It almost touches a larger boat containing the wire form of  $\text{CuO}$  which has been recently ignited. Several grams of  $\text{PbCrO}_4$  should be added to this or a following boat. The ends of the combustion tube should project a few inches from the outer wall of the furnace and should be covered by wicks of blotting paper which dip into suspended beakers  $\frac{3}{4}$  full of water.

The mixture of oxygen and carbon dioxide passes from the silica tube through 15-20 cubic centimeters of granulated  $\text{Zn}$ , and about the same amount of  $\text{CaCl}_2$  into the weighing bulb. This contains 30 per cent.  $\text{KOH}$  solution in a series of bulbs which are manufactured in a number of forms. Those having sealed on  $\text{CaCl}_2$  tubes are convenient, as some sort of weighable  $\text{CaCl}_2$  tube must follow the bulb tube. The former is protected by a second  $\text{CaCl}_2$  tube. Finally, an aspirator may be added to further regulate the flow of oxygen through the apparatus.

**Procedure No. 5.**—Weigh 2 grams of sample, place in a fairly compact mass in the groove of the boat, and after sweeping out the tube and weighing bulbs with oxygen for 15 minutes (the furnace being at  $1,000^\circ \text{C.}$ ), place the boat in

## Analysis of

**Sample No.**

[illegible]



the furnace as soon as the *weighed* bulbs have been replaced in position. In practice, the final weighing for one analysis serves as the initial weighing for the second, etc. Change in weight in KOH bulb  $\times 0.2727 \div 2 =$  per cent. C in steel. It is hardly necessary to use rubber stoppers for the ends of the absorption vessels during weighing, especially if the latter have restricted openings.

In addition to the above, the color method is often used. 0.2 gram of two steels of similar manufacture and character, the carbon content of one of which is known, are dissolved in equal volumes of C. P.  $\text{HNO}_3$  and the solutions are poured into two graduated colorimeter tubes. The unknown solution is then diluted until it is the same shade of brown or vice versa and the per cent. carbon calculated in terms of the water added. In practice the unknown is compared to a scale of known in comparison or test tubes.

### MANGANESE.

The bismuthate method is convenient for the determination of large or small quantities of manganese. It is based on the fact that  $\text{HMnO}_4$  is stable in  $\text{HNO}_3$  specific gravity 1.135 in the absence of  $-\text{Cl}$ . The method is generally applicable with the following precautions.  $-\text{Cl}$  must be rid of by boiling with  $\text{HNO}_3$ .  $\text{WO}_3$  of W steels must be filtered off after precipitation twice by evaporation to syrupy or dryness with aqua regia, and the latter replaced by  $\text{HNO}_3$ . Va and Cr must be precipitated by  $\text{CdCO}_3$  from a dilute  $\text{H}_2\text{SO}_4$  solution, and the latter replaced by  $\text{HNO}_3$  by boiling with concentrated acid and diluting.

One gram of sample is usually taken; solution in dilute  $\text{HNO}_3$  1-3 is used for steels,  $\text{H}_2\text{F}_2$  is added to silicious materials, and ores are fused with 10 grams  $\text{NaHSO}_4$ , 1 gram  $\text{Na}_2\text{SO}_3$ , and 0.5 gram  $\text{Na}_2\text{F}_2$ . An ether separation is advisable for alloy steels. (p. 24.)

**Procedure No. 6.**—Fuse or dissolve the sample, cool, add 0.5 gram of sodium bismuthate to the solution and heat till the pink color disappears. Clear the solution with sulfurous acid, heat to boiling to rid of excess of  $\text{SO}_2$  and cool.

Add about 3 grams bismuthate and agitate for a few minutes, but do not heat. Add 50 cubic centimeters water (containing 30 cubic centimeters  $\text{HNO}_3$  specific gravity 1.42 per liter), and filter off the bismuthate by running onto an asbestos or better a large alundum filter, and washing carefully. It is very convenient to

## Analysis of

**Sample No.**

[illegible]

use a one or two hole bell jar, and to suck the filtrate directly into the beaker. Run into the beaker a measured amount of standardized  $\text{FeSO}_4$  solution and titrate the excess with  $\text{KMnO}_4$  solution (1 gram per liter) which has been standardized best against a known Mn ore or steel.

$\text{FeSO}_4$  solution per liter: 12.4 grams  $\text{FeSO}_4$ , 25 cubic centimeters  $\text{H}_2\text{SO}_4$  specific gravity 1.84, 25 cubic centimeters glacial phosphoric acid.

### CONDITIONS FOR THE TITRATION OF IRON BY PERMANGANATE.\*

Iron is usually titrated with  $\text{KMnO}_4$ \* in a chlorid solution. (One gram of ore\*\* is dissolved in 15 cubic centimeters concentrated  $\text{HCl}$ , diluted, temperature being kept below  $100^\circ \text{C}$ . as  $\text{FeCl}_3$  is volatile; and unless the ore contains Ti, the solution is run through a reductor.) This titration of  $\text{Fe}^{\text{II}}$ — $\text{Fe}^{\text{III}}$  is subject to error from the following sources:

Improper standardization.

Side reactions of  $\text{KMnO}_4$ .

Tardy action of  $\text{KMnO}_4$ .

Iron wire is not thoroughly satisfactory for standardizing as the carbon in it forms hydrocarbons which reacting with the  $\text{KMnO}_4$  give results varying from 99.8-100.6 per cent. Fe.

Instead of Fe wire either a known iron ore (a known steel or a known solution of Mohr salt) or best of all 0.25-0.3 gram of  $\text{Na}_2\text{C}_2\text{O}_4$  of known quality may be used.

Procedure: dissolve some 0.3 gram of  $\text{Na}_2\text{C}_2\text{O}_4$  in 200-250 of hot water ( $80$ - $90^\circ \text{C}$ .) add 10 cubic centimeters concentrated  $\text{H}_2\text{SO}_4$  1-1, titrate with 0.560 per cent.  $\text{KMnO}_4$  to first trace of pink. The first 0.5 cubic centimeter and the last 0.5-0.8 cubic centimeter of solution should be added dropwise, and each drop allowed to decolorize before adding the next. Stir vigorously and continuously.

Burette delivery should be from 10-15 cubic centimeters per minute.

Final temperature should not be below  $60^\circ \text{C}$ .

\* Test problem.

\*\* A moisture test of the ore should be taken.

## Analysis of

**Sample No.**

[illegible]

The  $\text{KMnO}_4$  solution should have been filtered through asbestos and kept away from the light, and free from organic matter. It should be standardized frequently.

A gram of  $\text{NaOH}$  per liter may be added to insure stability.

When standardizing against a known ore, the conditions are more nearly those of actual titration of (1 gram) unknown samples. The following conditions must be observed:

Temperature must be at least  $70^\circ \text{C}$ .

The concentration of  $\text{HCl}$  must be not more than 60 cubic centimeters dilute acid specific gravity 1.04 per 150 cubic centimeters of solution, *i. e.*, 10 cubic centimeters  $\text{HCl}$  specific gravity 1.20 per titration.

The volume of the solution must be about 400 cubic centimeters per sample of about 0.4 gram  $\text{Fe}$ .

The beaker in which the titration is made should set on a white surface.

One gram of  $\text{MnSO}_4$  must be present else side reactions due to  $\text{HOCl}$  formation by  $\text{KMnO}_4$  will cause high results.

The addition of  $\text{H}_3\text{PO}_4$  (glacial, specific gravity 1.75) forms an almost colorless phosphate with the  $\text{Fe}$  and thus makes the end point more distinct.

Fifty cubic centimeters of the following solution is a convenient amount. 180 grams  $\text{MnSO}_4$  dissolved in 1,300 cubic centimeters water; 350 cubic centimeters  $\text{H}_2\text{SO}_4$  specific gravity 1.84; 350 cubic centimeters  $\text{H}_3\text{PO}_4$  specific gravity 1.75. By observing these precautions,  $\text{HOCl}$  will not be formed if the titration is carried on rapidly in warm acid solution. In cold or non-acid solution the reaction will not run quantitatively; *i. e.*, instead of



we find that the  $\text{MnO}_2$  of the  $\text{KMnO}_4$  will either oxidize some of the  $\text{HCl}$  or it will precipitate as  $\text{MnO}_2$ .

Upon solution, all the iron is in the ferric state. It is reduced to ferrous iron by adding 20 mesh  $\text{Zn}$  to the solution, and allowing it to dissolve completely, or better still, by sucking the solution through a column of 20 mesh  $\text{Zn}$  (previously

## Analysis of

**Sample No.**

[illegible]

amalgamated by stirring in a beaker with a 1 per cent.  $\text{HgCl}_2$  solution containing a globule of mercury) weighing about  $\frac{2}{3}$ -pound contained in a 1-inch glass tube. This tube (the Jones Reductor) should have a stop-cock at the base and be kept full of wash solution, when not in use. Wash solution = 50 cubic centimeters  $\text{H}_2\text{SO}_4$  specific gravity 1.84 per 2 liters water.

Solutions of  $\text{FeCl}_3$  should not be boiled as  $\text{FeCl}_3$  is appreciably volatile with steam.

If the end point is run by, add 1 cubic centimeter  $\text{FeSO}_4$  solution, titrate to pink, read, add another cubic centimeter  $\text{FeSO}_4$ , titrate to pink again, read, and deduct the difference between the two readings from the first reading.

Ores containing appreciable amounts of Ti cannot be reduced with Zn as the latter reduces the Ti also. The Ti is then oxidized by the  $\text{KMnO}_4$  causing high results. Such ores should be reduced by  $\text{SnCl}_2$ .

0.88 per cent.  $\text{K}_2\text{Cr}_2\text{O}_7$  solution may also be used for determining ferrous iron.  $\text{K}_2\text{Cr}_2\text{O}_7$  is used very little compared to  $\text{KMnO}_4$ . In this procedure the iron is dissolved in  $\text{HCl}$ ,  $\text{SnCl}_2$  solution is added during solution until finally a colorless (cooled) solution is obtained. The slight excess of  $\text{SnCl}_2$  in the cooled solution is oxidized with  $\text{HgCl}_2$  solution, and the iron titrated with either  $\text{KMnO}_4$  or more usually with  $\text{K}_2\text{Cr}_2\text{O}_7$ . This latter procedure involves the use of a tile covered with drops of very dilute fresh  $\text{K}_3\text{Fe}(\text{CN})_6$  solution. When the end point is approached drops of the titrated solution touched to the indicator with the tip of a stirring rod will give a faint and finally no blue color. This is the end point. Diphenylcarbazid may be used as an inside indicator.\* A potentiometer\* gives an excellent end point. (This may be done as **Optional Procedure No. A.**)\*

The insoluble residue from the  $\text{HCl}$  solution should always be filtered off; washed with hot dilute  $\text{HCl}$  and fused with  $\text{Na}_2\text{CO}_3$  or  $\text{KHSO}_4$ . Even colorless residues may contain Fe as phosphate. The Fe thus dissolved is added to the main solution. If none is found the residue is rejected.

Care must be taken in washing as cold or non-acid water allows the formation of insoluble Fe salts in the filter paper.

## Analysis of

**Sample No.**

[illegible]



# IRON ORES, IRON AND STEEL, LESSER CONSTITUENTS.

## NICKEL.

The dimethylglyoxime method for nickel is very accurate, and when the precipitate is dissolved and titrated, the method has the added advantage of rapidity. Furthermore, it is applicable to practically all steels containing nickel, to nichrome, to monel metal, to brasses and to German silver.

**Procedure No. 7.**—Dissolve in a large beaker 1 gram drillings in 20 cubic centimeters HCl 1-1 and add 10 cubic centimeters dilute  $\text{HNO}_3$ . Boil off excess of acids and add 30 cubic centimeters  $\text{H}_2\text{SO}_4$  containing a little  $\text{HNO}_3$ . Add 10-15 cubic centimeters powdered tartaric acid (citric acid may also be used), when all dissolved, make slightly alkaline with  $\text{NH}_4\text{OH}$ . Then add HAc until the solution reacts acid (if Ni only is wanted the most of the Fe may well be separated by ether from HCl solution specific gravity 1.100-1.105). Where-upon heat to boiling and add 5 times as much dimethylglyoxime by weight as 1 per cent. solution in alcohol as there is Ni in the sample. Make the solution alkaline with  $\text{NH}_4\text{OH}$ , and if convenient allow the precipitate formed to stand an hour before filtering into a gooch. There should be 4-5 times as much solution as there is precipitating solution added to prevent the solution of the latter and the precipitate in the former. The Ni precipitate should not be allowed to get cold.

In routine work, the precipitate may be filtered off at once into a weighed alundum or gooch crucible, washed with very dilute  $\text{NH}_4\text{OH}$  and with a little alcohol and weighed. Precipitation is 20.32 per cent. Ni.

The analysis may be further hastened by catching the precipitate on alundum or on a Büchner funnel covered with an asbestos mat, dissolving the precipitate in a little warm concentrated  $\text{HNO}_3$ , catching the solution (using a bell jar) in a beaker, boiling with a few grams  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and cooling with clean pieces of ice. The indicator is 10 cubic centimeters of 0.05 per cent.  $\text{AgNO}_3$ , plus 10 cubic centimeters 2 per cent. KI solution, and the titrating solution, 0.475 per cent. KCN solution which has been standardized against a steel, the Ni content of which is known.

## Analysis of

**Sample No.**

[illegible]

### COPPER.\*

**Procedure No. 8.**—3–5 grams of steel are dissolved in 7 cubic centimeters  $\text{H}_2\text{SO}_4$  diluted with 60 cubic centimeters water. Drop into the solution a piece of sheet Al  $1\frac{1}{2}$ -inch by  $1\frac{1}{2}$ -inch with turned over edges so that both sides will be exposed. Boil the solution 25 minutes to precipitate the Cu, and decant the solution through a filter, washing the Cu in the beaker with pure water. Rinse off the Al with dilute  $\text{HNO}_3$  and remove with a glass rod; place the beaker under the washed filter, poke a hole in the latter, and wash any adhering Cu into the beaker. Electrolyze the dissolved Cu, depositing on a gauze cathode previously weighed. 0.5-gram Cu will deposit quantitatively from a nitrate solution containing a few drops only excess of  $\text{HNO}_3$  in from 15 minutes to an hour if enough surface is provided. Add a few cubic centimeters  $\text{H}_2\text{O}_2$  solution towards the end of the deposition to rid of  $\text{HNO}_3$  in which Cu is somewhat soluble.

A 6-volt 100-ampere battery is a convenient source of current, a larger one is better; 110 volts direct current may also be used if suitable resistance is inserted in the circuit. For rapid determinations, using more than a small fraction of an ampere, plain electrodes and motionless solutions must be superseded by one of the following: Rotating the anode or cathode, rotating the solution by means of a small air jet or a solenoid, or increasing the surface of the electrodes by using Pt. (or Cu plated brass) gauze. If the gauze be used, there is not much saving in time in using rotating devices. A rheostat and meters are advisable.

The procedure details are to weigh the clean electrodes after washing it in distilled water followed by alcohol (and ether) and air blast or air bath drying; insert in the solution, electrolyze, decrease current, withdraw the electrode, while rinsing it with water, set in a beaker of pure water a minute, withdraw, rinse with alcohol (and ether), dry and weigh. Difference in weight is Cu.

Instead of precipitating with Al,  $\text{H}_2\text{S}$  may be used. The precipitate is filtered through a small paper washed with warm dilute  $\text{H}_2\text{SO}_4$ , ignited in porcelain, dissolved in  $\text{HNO}_3$ , transferred to a (weighed) Pt crucible, treated with  $\text{H}_2\text{F}_2$  and  $\text{H}_2\text{SO}_4$  and reweighed or dissolved in  $\text{H}_2\text{SO}_4$  or  $\text{HKSO}_4$  (warmed) and electrolyzed or determined colorimetrically. If Mo is present this last solution must be treated with  $\text{NaOH}$  to separate the copper as  $\text{CuO}$ . The  $\text{CuO}$  is filtered off and the Cu determined as above. The  $\text{CuO}$  is filtered from the filtrate as sulfid and roasted to oxid.

### TUNGSTEN.<sup>10</sup>

**Procedure No. 9.**—Two grams of the steel\* may be dissolved in dilute  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  in a casserole, and the  $\text{WO}_3$  precipitated by the addition of 60 cubic

\* W steels may be softened by annealing at  $700^\circ$  for 2 hours.

## Analysis of

**Sample No.**

[illegible]

centimeters  $\text{HNO}_3$  1.42. Digest the  $\text{WO}_3$  until it is of a clear yellow color: to the solution a little cinchonine solution\* is added if W only is wanted, (or else the solution is taken down to dryness. Redissolve in  $\text{HCl}$  1-1 to which 10 cubic centimeters concentrated  $\text{HNO}_3$  is added), dilute and filter. (Dissolve and adhering  $\text{WO}_3$  to casserole with a bit of filter paper dipped in  $\text{NH}_4\text{OH}$  and add to main precipitate) wash precipitate with water place in weighed platinum crucible and ignite, cool, weigh, treat with  $\text{H}_2\text{F}_2$  and  $\text{H}_2\text{SO}_4$ , reignite on a ring burner, cool and weigh.  $\text{WO}_3$  is volatile at bright red heat, hence both the above ignitions should be done carefully  $\text{WO}_3 \times 79.31 \div 2 = \text{W}$ . (Fusion with  $\text{HKSO}_4$  or  $\text{Na}_2\text{CO}_3$  is necessary to rid the precipitate quantitatively of iron.)

The  $\text{WO}_3$  being an acid anhydrid may be dissolved in  $\text{NaOH}$  and the excess of the latter titrated with standard  $\text{HCl}$  using phenolphthalein as an indicator, and standardizing against a steel the W content of which is known.

### CHROMIUM ONLY."

(Chromium may be determined by treating the  $\text{HCl}$  solution of 2 grams of steel as follows: The solution is evaporated to specific gravity 1.100-1.105 and the iron separated (twice), by shaking in a separatory funnel, with ether. Add  $\text{NH}_4\text{OH}$  to the water layer, filter, dry ignite and fuse with  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ . Extract with water, and wash with dilute  $\text{Na}_2\text{CO}_3$  solution giving  $\text{Na}_2\text{CrO}_4$  and some Al in the filtrate. Evaporate to syrupy with excess  $\text{NH}_4\text{NO}_3$ . Dilute and filter again, giving  $\text{Na}_2\text{CrO}_4$  only in the filtrate. Boil to rid of  $\text{NH}_4\text{OH}$  and reduce the Cr with  $\text{H}_2\text{SO}_3$ . Boil and add  $\text{NH}_4\text{OH}$  in excess, filter, wash, ignite and weigh the  $\text{Cr}_2\text{O}_3$  68.46 per cent. Cr.)

### VANADIUM ONLY."

For Ores: Dissolve 1 gram of ore in 25 cubic centimeters of the following: 300 cubic centimeters  $\text{HNO}_3$ , specific gravity 1.42; 300 cubic centimeters  $\text{H}_2\text{SO}_4$ , 1.84; 300 cubic centimeters water 100 cubic centimeters  $\text{H}_3\text{PO}_4$  specific gravity 1.75, 4-5 grams  $\text{MnSO}_4$ ; dilute and filter. To filtrate, add 1-gram sodium bismuthate, stir, heat to rapid boiling. Add a few cubic centimeters  $\text{HCl}$  and re-boil a moment. Cool, ice may be used, filter. Add a pipetteful of standardized

\* Twenty-five grams cinchonine in 200 cubic centimeters dilute  $\text{HCl}$  1-1.

## Analysis of

**Sample No.**

[illegible]

ferrous sulfate solution, and titrate with  $\text{KMnO}_4$ , running a known sample at the same time.

For Steels: No. 161 Bureau of Standards method involves the separation of Fe by absorption in a Hg cathode. (See p. 30.) The Cr is absorbed by the Hg, hence it cannot be determined in the same sample. Cr should be determined by Cain's method<sup>12</sup> as  $\text{PbCrO}_4$ , although the combined method, given below, if practiced becomes accurate enough for routine work.

### CHROMIUM AND VANADIUM IN STEEL. USUAL METHOD.<sup>13</sup>

**Procedure No. 10.**—Dissolve 2 grams of known and unknown steel (or 0.5-gram ferro) in 10 cubic centimeters  $\text{H}_2\text{SO}_4$  and 50 cubic centimeters water in a large beaker. Oxidize the solution by adding 60 cubic centimeters dilute  $\text{HNO}_3$  1-1 and boil to rid of nitrous fumes. Dilute to about 300 cubic centimeters and add enough  $\text{KMnO}_4$  solution (30 grams  $\text{KMnO}_4$  per liter) to keep precipitated a little  $\text{MnO}_2$  after boiling 20 minutes. Filter off the  $\text{MnO}_2$  and wash with very dilute  $\text{H}_2\text{SO}_4$ .

To filtrate, add standardized  $n/50$   $\text{FeSO}_4$  solution until the color of the solution changes to colorless or light green, add a few tenths of a cubic centimeter more, and titrate the excess with  $n/50$   $\text{KMnO}_4$ . (Fe equivalent of  $\text{FeSO}_4$  — Fe equivalent of  $\text{KMnO}_4$ )  $\times 0.3103$  = amount Cr. Better compare direct to standard.

Va. Add exactly 1 cubic centimeter of a 0.1 per cent. solution of  $\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  to the beaker and add the standard  $\text{FeSO}_4$  until the yellow shade of the Cr changes to a full green. Do not titrate to blue, but titrate the known and unknown to the same color or Fe equivalent  $\text{FeSO}_4 \times 0.914$  = amount Va. Better compare to standard. These colors are difficult to distinguish without practice.

### MOLYBDENUM.<sup>14</sup>

**Procedure No. 11.**—Dissolve 2 grams of steel in 50 cubic centimeters  $\text{HCl}$ , heat to boiling and add a little  $\text{HNO}_3$  to complete the solution and oxidize the Fe,

## Analysis of

**Sample No.**

[illegible]



but do not add excess. Evaporate to syrupy, add 50 cubic centimeters dilute HCl 1-3 filter off  $\text{WO}_3$  if present washing with dilute HCl. If much  $\text{WO}_3$  is present a second evaporation is advisable.

To the filtrate add dilute NaOH to neutralize nearly all the HCl, but do not add enough to cause the color of the solution to deepen. Transfer to a separatory funnel, and drop the solution into a 500 cubic centimeter graduated flask containing 150 cubic centimeters hot NaOH solution, 6 per cent., shaking the flask vigorously while dropping in the NaOH so that the  $\text{Fe}(\text{OH})_3$  formed will not carry down with it any Mo. Wash out the separatory funnel into the flask.

Dilute the solution to the 500 cubic centimeter mark, and filter through a large paper washing well. To 250 cubic centimeters of the filtrate, add HCl to acidity (methyl orange), add a few cubic centimeters more, followed by a few drops sulfurous acid to reduce Cr, and boil.

Add 10 grams AmAc stir to dissolve, add 40 cubic centimeters of a 1 per cent.  $\text{PbAc}_2$  solution, filter, dry the precipitate, separate, ignite paper, and bulk of precipitate and ignite both to faint redness in a weighed porcelain crucible. Two  $\times$  26.16 per cent. of precipitate is Mo.

A somewhat shorter method is to precipitate the Mo as  $\text{MoS}$  from dilute  $\text{H}_2\text{SO}_4$  solution, filter through asbestos, wash, dissolve the precipitate in aqua regia, and evaporate the solution with  $\text{H}_2\text{SO}_4$  (if Fe remains the  $\text{H}_2\text{S}$  treatment should be repeated), rid of Cu, if present with NaOH precipitate the Mo as  $\text{MoS}$  filter, wash and cautiously ignite to  $\text{MO}_3$ .

### TITANIUM.<sup>16</sup>

**Procedure No. 12.**—Dissolve 5 grams of known and unknown sample of iron in 40 cubic centimeters HCl specific gravity 1.05, dilute, filter and wash. The insoluble contains all the Ti. Ignite the paper and precipitate in a 20-gram Pt crucible and treat with  $\text{H}_2\text{F}_2$  and  $\text{H}_2\text{SO}_4$ . Fuse the residue with  $\text{Na}_2\text{CO}_3$ , dissolve the fusion in water, filter and dissolve the insoluble in  $\text{H}_2\text{SO}_4$  (if necessary  $\text{H}_2\text{SO}_4$ ) and combine the two solutions.

Add  $\text{H}_2\text{O}_2$  to both the known and the unknown solutions and compare in a

## Analysis of

**Sample No.**

[illegible]

colorimeter. If a Fe free Ti solution is used for a standard, ferric alum should be added to it to match the iron color of the unknown, before  $\text{H}_2\text{O}_2$  is added to either.

Ores may be fused with  $\text{Na}_2\text{CO}_3$  the washed residue after dilute HCl treatment fused with  $\text{H}_2\text{SO}_4$  and Ti determined colorimetrically in the latter dissolved fusion. Ferros are best determined by one of the gravimetric processes.

### ALUMINIUM.<sup>16</sup>

**Procedure No. 13.**—The chlorid solution of 5 grams of steel is evaporated with  $\text{H}_2\text{SO}_4$  to small bulk, diluted to 200 cubic centimeters and almost neutralized with  $\text{NH}_4\text{OH}$ . The solution is then poured into a medium sized beaker containing a layer of about 300 grams Hg and a contact in the form of a sealed in Pt wire at the base, (or else a glass tube passing down through the solution, with a sealed in Pt wire at the lower end, containing either Hg or a place of Cu wire attached to the inside end of the Pt wire), forming the electrical contact between the current supply and the Hg cathode.

The Fe is driven in to the cathode (with a rotating anode a current of several amperes may be used and the Fe rid of in an hour) leaving Al, P, and Ti only in solution. Precipitate twice with  $\text{NH}_4\text{OH}$  and ignite and weigh in a porcelain crucible. The  $\text{P}_2\text{O}_5$  should be determined in another sample, the above residue examined colorimetrically for Ti as  $\text{TiO}_2$ , and these deducted giving total  $\text{Al}_2\text{O}_3$ .

Peters method is not recommended for the determination of  $\text{Al}_2\text{O}_3$ . The latter may be obtained by a phenylhydrazone precipitation, by an ether separation followed by acetate separation and ammonia precipitation, or finally the electrolytic procedure may be used.

## Analysis of

**Sample No.**

[illegible]

# LIMESTONES, SLAGS AND CLAYS."

## LIMESTONES.

**Procedure No. 14—Insoluble Silicious Matter.**—Boil 1 gram of limestone in a beaker with 5 cubic centimeters HCl and 1 cubic centimeter HNO<sub>3</sub> plus 25 cubic centimeters H<sub>2</sub>O until action ceases. Wash off cover glass into beaker and evaporate solution to dryness. Redissolve in 10 cubic centimeters concentrated HCl diluted with 50 cubic centimeters H<sub>2</sub>O. Filter. Save filtrate; wash precipitate well with hot water, ignite and weigh. Examine for metals. If SiO<sub>2</sub> is wanted, baking, followed by solution and H<sub>2</sub>F<sub>2</sub> treatment are necessary.

**Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.** Heat the filtrate to boiling, add slight excess NH<sub>4</sub>OH. Boil a few minutes, filter and wash. Dissolve precipitate in a little HCl on the paper, wash and let the always slightly acid solution run into a small beaker. Reprecipitate with slight excess NH<sub>4</sub>OH, filter, wash, ignite and weigh as Fe<sub>2</sub>O<sub>3</sub>; Al<sub>2</sub>O<sub>3</sub>. Fe may be titrated with KMnO<sub>4</sub> after running the HCl solution through a reductor.

**CaO.** Unite the two filtrates, heat to boiling, add 25 cubic centimeters 5 per cent. (NH<sub>4</sub>)<sub>2</sub> C<sub>2</sub>O<sub>4</sub> solution. Digest on the steam bath as long as convenient up to 1 hour. Filter, wash with hot water. Either ignite to CaO in a weighed Pt crucible or else after washing the precipitate into 100 cubic centimeters warm water, by poking a hole in the filter paper; and adding 30 cubic centimeters N/10 H<sub>2</sub>SO<sub>4</sub> to the filtrate to form H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, titrate with KMnO<sub>4</sub>.

**MgO.** To the above filtrate add 30 cubic centimeters saturated solution microcosmic salt. Acidulate with HCl, and evaporate to not more than 300 cubic centimeters. Cool the still acid solution. Add NH<sub>4</sub>OH to alkalinity (litmus). Add 5 cubic centimeters NH<sub>4</sub>OH, and digest on the steam bath, or stand over night. Filter and wash with dilute NH<sub>4</sub>OH. Dry and separate from paper onto glazed paper, burn filter paper on a platinum wire over a weighed porcelain crucible; combine the precipitates and weigh as Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. 36.22 per cent. MgO.

A moisture test at 100° C. and a loss on ignition test at the temperature of the blast lamp should be made on separate 1 gram specimens of the limestone.

## Analysis of

**Sample No.**

[illegible]

Ca can generally be determined by solution in HCl, evaporation to dryness (to separate  $\text{SiO}_2$ ) re-solution in HCl, precipitation of Fe and Al by  $\text{NH}_4\text{OH}$ ; and precipitation of  $\text{Ca}^{++}$  with  $--\text{C}_2\text{O}_4$ . This may be weighed or titrated.

Ca and Mg may be determined in the same solution as follows:<sup>18</sup> Precipitate the  $\text{SiO}_2$ , Fe and Al as above using a slight excess only of  $\text{NH}_4\text{OH}$ . To the filtrate, add excess  $\text{H}_2\text{C}_2\text{O}_4$  solution followed by dilute  $\text{NH}_4\text{OH}$  to alkalinity (litmus). Add enough ammonium arsenate to precipitate the Mg and add  $\text{NH}_4\text{OH}$  constantly stirring the hot solution until the magnesium ammonium arsenate comes down; i. e., about 10 cubic centimeters concentrated  $\text{NH}_4\text{OH}$ . Cool add 10 cubic centimeters more  $\text{NH}_4\text{OH}$ .

Ca is determined as follows: The ammonium arsenate solution should be added right after the oxalic acid so that Mg may not precipitate as oxalate. Let stand 20 minutes (up to 12 hours) and filter on paper and wash with dilute ammonia water. Transfer washed precipitate to  $\frac{1}{4}$  or  $\frac{1}{2}$ -liter Erlenmeyer, washing with hot water followed by 1 per cent.  $\text{H}_2\text{SO}_4$  to dissolve. Make up the volume in the flask to 74.80 cubic centimeters and add 10 cubic centimeters 1-1  $\text{H}_2\text{SO}_4$ . Heat to  $75^\circ \text{C}$ ., and titrate with 0.566 per cent.  $\text{KMnO}_4$  solution. Standardized with Ca and Mg precipitated under the same conditions.

Mg. Cool the Erlenmeyer in which the titration was made, add 25 cubic centimeters 1-1  $\text{H}_2\text{SO}_4$ , bulk equalling about 125 cubic centimeters; add 5 grams powdered KI slowly and immediately titrate to straw color with 1.9 per cent.  $\text{Na}_2\text{S}_2\text{O}_3$  solution, titration taking 8 minutes. Standardize the  $\text{Na}_2\text{SO}_3$  against  $\text{MgO}$ , Mg ribbon, or best against a known limestone as above.

Finally, the Mg may be determined volumetrically using a milli-voltmeter as an indicator. This procedure is extremely rapid and valuable. It should be studied by the reader, but attempted only by those familiar with elementary electrochemistry.

**Optional Procedure No. B.**—The HCl solution of the limestone<sup>19</sup> is titrated with NaOH and the constancy of concentration of  $[\text{H}]^+$  or  $-\text{[OH]}$ , (measured on the millivoltmeter and plotted as ordinate) due to the precipitation of  $\text{Mg}(\text{OH})_2$  is plotted on paper or automatically, against the standardized alkali added (as abissa).

## SLAGS.

**SiO<sub>2</sub>.** See p. 3.

**Cu.** Disintegrate with HCl followed by  $\text{HNO}_3$ . Dehydrate  $\text{SiO}_2$  with  $\text{H}_2\text{SO}_4$  boiling solution to fumes, cool, dilute and filter off. Neutralize  $\text{H}_2\text{SO}_4$  with  $\text{NH}_4\text{OH}$  to only slight acidity, and throw down the Cu with Al. This latter should be Fe free or else the Fe in it determined carefully.

**Fe.** The Fe if present is, after reduction in the filtrate as  $\text{Fe}^{II}$ . This may be titrated or oxidized with Br or  $\text{HNO}_3$  and precipitated with  $\text{NH}_4\text{OH}$ .

## Analysis of

**Sample No.**

[illegible]



**Ca.** Ca may be determined in the last filtrate, but is more usually determined as follows. The solution freed from  $\text{SiO}_2$  and oxidized with Br or  $\text{HNO}_3$ , add  $\text{NH}_4\text{OH}$  to the first trace of  $\text{Fe}(\text{OH})_3$ . Add only enough hot saturated  $\text{H}_2\text{C}_2\text{O}_4$  solution to dissolve this, and add  $\text{NH}_4\text{OH}$  in slight excess. Add dilute warm  $\text{H}_2\text{C}_2\text{O}_4$  to just dissolve the  $\text{Fe}(\text{OH})_3$ , leaving the precipitate of  $\text{CaC}_2\text{O}_4$  in a clear yellowish green solution. Digest as long as convenient, decant through the filter, wash precipitate, and dissolve into a beaker with warm dilute  $\text{H}_2\text{SO}_4$ . Dilute to 200 cubic centimeters add 30 cubic centimeters, 10 per cent.  $\text{H}_2\text{SO}_4$ , and titrate with 0.569 per cent.  $\text{KMnO}_4$  solution standardized against a known slag.

### **$\text{Na}_2\text{O}$ AND $\text{K}_2\text{O}$ IN CLAYS.**

**Procedure No. 15.**—The J. Lawrence Smith method for clays. Mix 1-gram clay with 1-gram  $\text{NH}_4\text{Cl}$  in a porcelain mortar, grinding thoroughly. Add 8 grams of powdered  $\text{CaCO}_3$ , alkali free, and regrind. Pour into a 40 gram Pt crucible, lined with a little powdered  $\text{CaCO}_3$ , and sweep out the mortar with a little more  $\text{CaCO}_3$ , adding this to the charge. Place the crucible  $\frac{3}{4}$  through a piece of punched asbestos board, and put on cover.

Heat the crucible gently with the tip of a Bunsen flame until the  $\text{NH}_3$  is all driven off. Then heat for  $\frac{3}{4}$ -hour at full red heat. Cool, the melt and transfer quantitatively, washing with water, to a casserole. Digest the charge thoroughly, filter and wash with hot water until the filtrate amounts to 250 cubic centimeters.

To the hot filtrate, containing all the alkalis as chlorids, add  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  in excess; digest a short while, and filter off the  $\text{CaCO}_3$ . Wash latter with water containing a little  $\text{NH}_4\text{OH}$ , concentrate the filtrate to small volume in silica or platinum, transfer to a Pt crucible, and ignite to dryness, using a ring burner. Weigh as  $\text{NaCl} + \text{KCl}$ . The chlorids should be white, and should leave no residue on solution in 10 cubic centimeters water. Add excess  $\text{H}_2\text{PtCl}_6$  solution, evaporate again to syrupy carefully. Add 20 cubic centimeters, 80 per cent.  $\text{C}_2\text{H}_5\text{OH}$ , and let stand until the Pt salts dissolve. Filter through a weighed gooch and wash the  $\text{K}_2\text{PtCl}_6$  with 80 per cent.  $\text{C}_2\text{H}_5\text{OH}$ , dry and weigh.  $\text{K}_2\text{PtCl}_6$  is 19.38 per cent.  $\text{K}_2\text{O}$ . Eighty per cent.  $\text{C}_2\text{H}_5\text{OH}$  should be used and the  $\text{Na}_2\text{PtCl}_6$  given time to dissolve.

## Analysis of

**Sample No.**

[illegible]

# NON FERROUS ALLOYS."

## BRASS, BRONZE, GERMAN SILVER, SOLDER, BEARING METALS.

Brass consists of Cu, Zn, Pb, Sn, (Fe, Al, Mn, P, Ni in small amounts).

Bronze consists of Cu, Sn, Zn, (P, Mn, Pb sometimes).

German Silver consists of Ni, Cu, Zn, Fe, Mn, (Co).

Solder consists of about half and half Pb and Sn, carrying a fraction of a per cent. of Sb, Zn, Cu and Bi.

Bearing metals consist of Pb, Sb, Cu, Sn, (Zn).

The above compositions are only approximate, and often overlap. Unusual constituents are often found, being added to impart certain specifications, or finding their way into the charge by accident.

### BRASS.

**Procedure No. 16.**—Dissolve 1 gram of sample in 20 cubic centimeters  $\text{HNO}_3$  1-1, and digest at about  $90^\circ \text{C}$ . for from 15-90 minutes. If the Sn content is less than 10 per cent. the hydrated  $\text{SnO}_2$  formed\* will generally be as pure\*\* as the limit of accuracy of the entire analysis requires. Filter through paper or weighed alundum, wash with hot water containing a little  $\text{HNO}_3$ , ignite and weigh as  $\text{SnO}_2$  78.81 per cent. Sn.

**Pb. Cu.** Electrolyze the filtrate, (if it contains no Mn,) after boiling off almost all the  $\text{HNO}_3$ , and diluting to about 150-200 cubic centimeters. A Pt gauze anode and cathode are advisable. Rotation of the solution is convenient, but not necessary.\*\*\* As mentioned on p. 22 a difference of potential of about 6 volts and

\* Two to three cubic centimeters of a solution of egg albumin (white of one egg beaten with about 100 cubic centimeters water) will cause fine  $\text{SnO}_2$  precipitates to coagulate.

\*\* The purification is described under bronze.

\*\*\* Current density is the ratio of the current-strength to the area of the electrode surfaces. A current-strength of one ampere per 100 square centimeters is the unit. The usual gauze cathode will allow  $1 - 2 \times$  the unit current density called N.D.<sub>100</sub>, but by rapid rotation up to 15 amperes may be used per 100 square centimeters of gauze surface, i. e.,  $\text{N.D.}_{100} = 15$ . (Texts of Smith and Classen.)

Decomposition potential is the lowest potential which will allow a permanent plate of metal to deposit in a given solution. It is about 2 volts for most ordinary salts. Since such a low potential will not always allow a very large current to flow through the bath, it is customary to employ a battery of at least three lead storage cells in series.

## Analysis of

**Sample No.**

[illegible]

a current of 0.5-6 amperes is necessary. Add 1-2 cubic centimeters  $\text{H}_2\text{O}_2$  solution towards the end of the deposition.

The Pb deposits as  $\text{PbO}_2$ , 86.4 per cent. Pb on the anode. The anode is dipped in pure water, dried at about  $230^\circ \text{C}$ . and weighed. ( $\text{PbO}_2$  is dissolved in  $\text{HNO}_3$  to which  $\text{H}_2\text{O}_2$  solution,  $\text{C}_2\text{H}_5\text{OH}$  or  $\text{H}_2\text{C}_2\text{O}_4$  solution has been added.) The Cu precipitates as metals on the cathode; it is washed with pure water dried with  $\text{C}_2\text{H}_5\text{OH}$  and  $(\text{C}_2\text{H}_5)_2\text{O}$  at  $90^\circ \text{C}$ . cooled and weighed. The electrolysis should take from 15-90 minutes depending on the current, electrodes and sample. Currents as high as 8-15 amperes have been used, and 0.5-gram Cu deposited in 10 minutes. Thirty-four minutes is a conservative time for the deposition of the Cu in 1-gram brass using gauze electrodes, 2-4 amperes, rotation by means of a solenoid, motor or air blast.

Pb is also determined as sulphate, by boiling off the  $\text{HNO}_3$  (in which  $\text{PbSO}_4$  is slightly soluble), diluting the solution and pouring into dilute  $\text{H}_2\text{SO}_4$ . The same conditions as those for the  $\text{BaSO}_4$  precipitation should be noted. Twenty cubic centimeters alcohol should be added to bring down the last of the  $\text{PbSO}_4$ .  $\text{PbSO}_4$  should not be ignited in platinum.

The following was given by the Bureau of Standards.

" . . . the tin . . . (about 1 per cent. of brass sample No. 37) . . . contained impurities to the amount of 0.05-0.08 of 1 per cent., principally Fe, with some Cu, etc." (*This is beyond the limit of accuracy of the Cu determination. Therefore the  $\text{SnO}_2$  needs no further purification unless present in large amounts. Bureau uses 1-1  $\text{HNO}_3$ .*)

"It is believed that the  $\text{PbSO}_4$  gives the nearer actual Pb content. . . . the impurities in the  $\text{PbO}_2$  are greater than the difference between the Pb obtained as  $\text{PbSO}_4$  and the Pb obtained as  $\text{PbO}_2$ ."

When the Cu is all deposited from the solution (best determined by a calomel electrode and a mille-voltmeter),\* the electrodes are washed off into the solution and the following procedures gone through.

**Fe.** The sample is now examined for Fe by adding slight excess  $\text{NH}_4\text{OH}$  filtering, and determining the washed precipitate as  $\text{Fe}_2\text{O}_3$  or dissolving, reducing and titrating with  $\text{KMnO}_4$ .

\* Wait until you are sure all the Cu is deposited, and then wait three minutes more.

## Analysis of

**Sample No.**

[illegible]

**Ni.** Ni is determined as dimethylglyoxime. It is advisable to dissolve this and reprecipitate to clear of Zn. The conditions for the precipitation are given on p. 20. Tartaric acid need not be used. (Ni may be plated from a slightly alkaline with  $\text{NH}_4\text{OH}$  solution, although Fe, if present, will also be carried down, by the current, and hence must first be separated.)

**Zn.** From the solution freed from Ni and Fe as above the Zn is separated by one of three methods.<sup>21</sup> Titration with  $\text{K}_4\text{Fe}(\text{CN})_6$  solution, precipitation as phosphate, or deposition by the electric current. (Zn is sometimes precipitated as  $\text{ZnS}$  and roasted to oxid, but this compared with the above is rare.)

All determinations of Zn are best carried on in pure solution, subject to the following conditions.

**Electrolysis.** Boil off  $\text{NH}_4\text{OH}$  with  $\text{HNO}_3$  and rid of latter with  $\text{H}_2\text{SO}_4$  boiling to first fumes. Dilute to about 150-200 cubic centimeters and add 5-12 grams solid  $\text{KOH}$  to the solution. Electrolyze the heated complete solution using a solenoid or a rotating cathode and up to 5 amperes. A cathode of either Ni or Cu plated No. 100 brass gauze should be used. Platinum is not altogether suitable. The following precautions should be observed in Zn electrolysis.

All acids except  $\text{H}_2\text{SO}_4$  should be absent. Only a little excess  $\text{H}_2\text{SO}_4$  should be present, as alkali sulfates are not very soluble in alkaline solution.

Zn is lost during the washing off of the cathode with water. The formation of  $\text{Zn}(\text{OH})_2$  about makes up for this, if the washing is done rapidly and carefully. The procedure is to remove the electrode from the bath, dip into distilled water, and twirl rapidly between the fingers.

Drying is accomplished by dipping in  $\text{C}_2\text{H}_5\text{OH}$  then in  $(\text{C}_2\text{H}_5)_2\text{O}$  and drying above room temperature at about  $80-90^\circ \text{C}$ . over a hot plate. Else  $\text{Zn}(\text{OH})_2$  will form.

The anode is best placed above the cathode. The latter or the solution should be rotated. Anode rotation is not satisfactory.

Time of electrolysis, about 40 minutes.

At end of 30 minutes, add ice to cool the solution. (As above, the addition

## Analysis of

**Sample No.**

[illegible]



of the solid KOH heats the solution to about the right temperature for most of the electrolysis.)

Nitrates, chlorids and  $\text{NH}_4$  salts should be absent.

The following remarks of Sand<sup>2a</sup> especially those on cooling, apply to zinc deposition by electrolysis. "The formation of crystals is almost always bound up with the intermediate formation of a metastable state. Thus crystallization from a solution is probably always connected either with local supersaturation or with the intermediate production of an undercooled liquid. In a similar way, it seems very probable that metal deposits are produced electrolytically in the first instance in a metastable state, and that it depends on the ease and rapidity with which this state is destroyed whether a fine or a coarse grained deposit will result."

**Precipitation.** The gravimetric procedure for Zn in pure solution is as follows: Add to the Zn solution as chlorid or nitrate, bulk about 150 cubic centimeters,  $\text{NH}_4\text{OH}$  to slight alkalinity. Add a drop of litmus solution and drop in  $\text{HNO}_3$  1-5 till the color just changes to red. Exact neutrality must be reached.

Heat the solution and pour in  $(\text{NH}_4)_2\text{HPO}_4 = 12 \times$  the weight of Zn present. This is prepared from the commercial salt by adding to its solution,  $\text{NH}_4\text{OH}$  until a drop of phenolphthalein just turns pink. The object is to get exact neutrality, as here also the precipitate is soluble in both acid and alkali.

Digest the resulting precipitate on the steam bath for 30 minutes, and let stand for 4 hours or longer until the precipitate is decidedly crystalline. Filter into a weighed porcelain gouch, wash with  $(\text{NH}_4)_2\text{HPO}_4$ , ignite cautiously, until free from  $\text{NH}_3$  and then at dull redness for 15 minutes. Weigh as  $\text{Zn}_2\text{P}_2\text{O}_7$ , 42.89 per cent. Zn.

**Titration.** The Zn may be titrated with 2.2 per cent.  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  solution using 1 per cent.  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution, dropped on a wax coated tile, as an indicator. Standardize against 0.2 gram portions of ZnO dissolved in HCl. The conditions for this titration are discussed fully under Zn ores (pp. 60-62) and should be carefully studied before attempting a titration. Furthermore, it is well to try several titrations using a  $\text{ZnCl}_2$  solution in order to acquire the technique of the process.

Determine the Zn in the filtrate from the Fe and Ni of the brass sample by one of the methods given above.

## Analysis of

**Sample No.**

[illegible]

**BRONZE.**

**Sn only. Procedure No. 17.**—The analysis of 1 gram of bronzes offers no great difference in procedure from the above except that the  $\text{SnO}_2$  must be purified by fusion with a mixture of equal parts of S and  $\text{Na}_2\text{CO}_3 = 6$  times the weight of the  $\text{SnO}_2$ . Dissolve the cooled melt in hot water. The polysulfids of the other metals are reduced with  $\text{Na}_2\text{SO}_3$  solution and the metals thus precipitating are filtered, washed and added to the main filtrate. The Sn remains in solution and may be precipitated as metal on a Cu plated Pt cathode. (Add 4 grams KCN to keep S in solution.) Or, better still, the foreign sulfids are ignited cautiously to oxids and weighed before dissolving and adding to the main solution. Their weight is deducted from the total weight of the impure  $\text{SnO}_2$ .

**Optional Rapid Procedure No. C.**—The rapid analysis of Bronze is accomplished as follows: Dissolve 1 gram in aqua regia, boil off Cl, take up in 15 cubic centimeters HCl 1-3, dilute to 150 cubic centimeters, add 2 grams  $\text{NH}_2\text{OH.HCl}$  and electrolyze, keeping the cathode potential at  $-0.40$  volt against a calomel electrode, using a centi or millivoltmeter. The Cu will deposit in about 40 minutes using rapid stirring and gauze electrodes and the end point is clearly seen by the increase in cathode potential. Whereupon the current is decreased and finally shut off.

Weigh the washed, and dried with  $\text{C}_2\text{H}_5\text{OH}$  and  $(\text{C}_2\text{H}_5)_2\text{O}$ , cathode. Difference between the initial and this weighing  $\times 100 =$  per cent. Cu. Replace in the solution and after adding 3 grams more  $\text{NH}_2\text{OH.HCl}$  electrolyze (40 minutes) until no Zn is found with  $\text{H}_2\text{S}$ . In replacing the Cu plated cathode for the Sn deposit it should not set quite so deep in the solution as before. This prevents the Sn deposit coming directly in contact with the Pt and alloying with it.

In practice, most bronzes contain Zn (sometimes Pb) in addition to Cu and Sn, but the details of the rapid separation of these three or four elements from HCl solution have not yet been published.

Phosphor bronzes must be dissolved in  $\text{HNO}_3$ , and the  $\text{SnO}_2$  + impurities weighed. The Sn or impurities determined as under bronze, and the P determined as follows: Fuse the  $\text{SnO}_2$  from 3-10-gram sample of the bronze with KCN to form potassium phosphate, boil under hood, rid of Sn with  $\text{H}_2\text{S}$ , filter concentrate filtrate to 50 cubic centimeters, boil with Br water and precipitate the P with either

## Analysis of

**Sample No.**

[illegible]

molybdate mixture from a  $\text{HNO}_3$  solution or better with 10 cubic centimeters magnesia mixture\* per each 0.1 gram  $\text{P}_2\text{O}_5$  precipitated = 27.87 per cent. P.

**Mn** may be determined in bronze as follows: In absence of P dissolve bronze in  $\text{HNO}_3$ , filter, precipitate Pb as  $\text{PbSO}_4$ , details above, and electrolyze the filtrate. The Mn will deposit on the anode. Dissolve it off with  $\text{HNO}_3$  and either perhydrol solution or a reducing agent, and determine the Mn as per the bismuthate method from the boiled  $\text{HNO}_3$  solution. For other details and other bronzes, the larger books on the subject should be consulted.

German silver may be analyzed as follows: 1 gram is dissolved in  $\text{HNO}_3$ , boiled, Cu and Mn precipitated by electrolysis, and Mn, dissolved from the anode, may be determined by the bismuthate method. The Ni in the electrolysis filtrate is next determined as glyoxime, keeping the Fe in solution with HTr. Or the Fe may be separated by double precipitation with  $\text{NH}_4\text{OH}$ , and the Ni (and Co) determined by electrolysis from the ammoniacal solution. These are separated by dimethylglyoxime followed by nitroso-beta-naphthol. The Fe is determined (after decomposing the HTr if used, with boiling  $\text{HNO}_3$  or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  by  $\text{NH}_4\text{OH}$  before or after the Ni (and Co if present). Finally the Zn is determined from the evaporated filtrate, by one of the methods described elsewhere.

Monel metal may be analyzed as follows: 0.5-gram dissolved in  $\text{HNO}_3$ , the Cu determined by electrolysis, the Fe precipitated by  $\text{NH}_4\text{OH}$ , and the Ni determined by electrolysis in the filtrate. Or Cu may be separated with  $\text{H}_2\text{S}$ , and determined by roasting to oxid, Ni determined as dimethylglyoxime, and the Fe determined in the filtrate after destroying the tartaric acid with boiling  $\text{HNO}_3$  or  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Other methods are described in Johnson.

When alloys contain large amounts of Ni, samples weighing only a few tenths of a gram should be taken for the dimethylglyoxime determination. If this precipitate weighs much more than 0.1-gram or if it gets cold, it becomes hard to handle. It is 20.31 per cent. Ni. Conditions for determination are given on p. 20.

### BEARING METALS.\*

The following procedure is recommended by Demorest. Zn must be determined in a separate sample after precipitation of the other elements with  $\text{H}_2\text{S}$ .

**Procedure No. 18.**—Dissolve 1 gram of sample in 20 cubic centimeters  $\text{H}_2\text{SO}_4$ , specific gravity 1.84 in a  $\frac{1}{4}$ -liter Erlenmeyer, cool carefully, dilute to 70 cubic centimeters, reboil a few minutes and filter (preferably through a weighed alundum cone). The precipitate should be pure white, and the general conditions

\* Magnesia mixture. Eleven parts  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 28 parts  $\text{NH}_4\text{Cl}$  both in 130 cubic centimeters  $\text{H}_2\text{O}$ . To this add 7 grams  $\text{NH}_4\text{OH}$ . Settle over night and decant or filter for use.

## Analysis of

**Sample No.**

[illegible]

under  $\text{BaSO}_4$ , page 6, noted. The porcelain or alundum crucible containing the  $\text{PbSO}_4$  should be suspended inside another. (Two small ring stand rings, the upper wound with bits of Pt wire where the alundum or porcelain touches are suitable.) Ignite the crucibles, the inner one becoming a dull red, continuing the ignition for about 25 minutes.  $\text{PbSO}_4 = 68.31$  per cent. Pb. Or the Pb from  $\text{PbSO}_4$  may be determined electrolytically as under Pb, p. 64.

**Sb.** Make up the filtrate to 120-140 cubic centimeters heat to about  $80^\circ \text{C}$ . and titrate about 0.5 cubic centimeter beyond the end point with 0.569 per cent.  $\text{KMnO}_4$ . Titrate back with equivalent  $\text{FeSO}_4$  solution, to the usual pink end point. (The last of the Sb is hard to oxidize, hence the excess  $\text{KMnO}_4$ —mass action—is necessary. The excess is determined with  $\text{FeSO}_4$  solution.) The  $\text{KMnO}_4$  should be standardized against a warm dilute  $\text{H}_2\text{SO}_4$  solution of pure Sb, using equivalent  $\text{FeSO}_4$  solution to titrate back with.

**Cu.** Cu is determined in the same solution after the  $\text{KMnO}_4$  has been added, as follows: Add 3 grams HTr to keep Sb from precipitating, make slightly alkaline with  $\text{NH}_4\text{OH}$ , add 2 cubic centimeters  $\text{H}_2\text{SO}_4$ , and heat to boiling. Reduce  $\text{Cu}^{++}$  to  $\text{Cu}^+$  with 2 grams powdered  $\text{Na}_2\text{SO}_3$ , and when the latter has dissolved, precipitate the Cu with 10 cubic centimeters of 10 per cent. KCNS solution. Filter, wash well with water containing a small amount of KCNS per liter, and ignite the Cu salt to  $\text{CuO}$  in a weighed porcelain crucible.

**Other methods of Cu determination.** Dissolve the  $\text{CuCNS}$  in  $\text{HNO}_3$  and titrate with I solution. Dissolve the  $\text{CuCNS}$  in  $\text{NaOH}$  solution and titrate  $\text{HCNS}$  with  $\text{KMnO}_4$  solution. Dissolve the ignited  $\text{CuO}$  and determine the Cu by electrolysis or by colorimetric methods.

**Sn.** The Sn content of the alloy may be determined as follows: Proceed as through Sb on another sample (the same sample if it contains no Cu), add 50 cubic centimeters  $\text{HCl}$  and transfer the solution to a 500 cubic centimeter flask, making up to about 200 cubic centimeters. This flask should be provided with a 4-hole rubber stopper. Illuminating gas or  $\text{CO}_2$  bubbles through the solution and out through holes Nos. 1 and 3. The elongated tip of the burette passes through No. 2, and a rod of pure Fe, with the end bent into a coil passes through No. 4.

## Analysis of

**Sample No.**

[illegible]



Set up the flask above a Bunsen. Boil while passing gas through the solution—in which the Fe coil dips—until the solution becomes colorless. Slip up the Fe ring from the solution, and titrate the reduced Sn with N/10 iodine solution using a little starch solution as an indicator. The iodine solution should be standardized against 0.2-gram Sn, to which 0.15-gram Sb has been added. The procedure is then the same as for the sample.

Iodine solution. 6.5 grams or 13 grams iodine (resublimed from KI) dissolved in 50 cubic centimeters  $H_2O$  containing 12 or 20 grams KI diluted to 1 liter. Corresponding  $Na_2S_2O_3$  solution contains respectively 12.5 or 25 grams of thiosulfate.

A permanent starch solution may be made up by stirring 5 grams of starch into 200 cubic centimeters of cold water, heating to boil with constant stirring until the starch is thoroughly dissolved. Dilute with cold water to one liter and add 10 grams of crystallized  $ZnCl_2$ . Settle over night and decant for use.

Starch solution. Add 1-gram starch plus 5 grams  $H_2O$  after mixing thoroughly to 1 liter boiling water. Let stand, and use 2-3 cubic centimeters of the decanted solution.

Sn may be determined in tin plate by placing a definite fractional part of the total area of the plate in a tumbler  $\frac{2}{3}$  full of 40 per cent. Pb (Ac) $_2$  solution. The sample is dried and weighed before immersion, and after immersion the Pb carefully washed off. The final weight of the dried sample deducted from the initial  $\div$  the fraction of the total gives the weight of Sn on the sheet.

Sn may be separated from Sb (and Cu if present) by adding  $H_2S$  to a boiling oxalate solution of the metals for 45 minutes. Sn only remains in solution, and may be deposited on a copper plated cathode. 10 grams  $H_2C_2O_4$ , 10 grams  $(NH_4)_2C_2O_4$  in 200 cubic centimeters  $H_2O$  form the solution.

## Analysis of

**Sample No.**

[illegible]

# MATTE AND ORES.

## MATTE.

**S**, see p. 8.

**Pb**, if present, will precipitate as sulphate on boiling off the acids and gases (see below) with  $\text{H}_2\text{SO}_4$ . It is determined according to the methods on pp. 38 and 62.

**Cu**. 0.5–1 gram of the matte is dissolved in 15 cubic centimeters  $\text{HNO}_3$ , specific gravity 1.42, pulverized  $\text{KClO}_3$  added until all the sulfur is oxidized (to prevent inclusion of metals), and the solution boiled to beginning of fumes with 4.5 cubic centimeters  $\text{H}_2\text{SO}_4$ . **Pb** if present is filtered off from the diluted solution at this point and determined as per the preceding paragraph. The dilute **Pb** free solution is now electrolyzed for **Cu** after adding a few cubic centimeters  $\text{HNO}_3$ .\* A few cubic centimeters  $\text{H}_2\text{O}_2$  solution are added toward the end of the electrolysis, as noted under brass.

Copper may also be determined by adding strips of **Al** to the **Pb** free solution after almost neutralizing (litmus) with  $\text{NH}_4\text{OH}$ , and determining the copper as in steel, p. 22.

**Fe, Zn**. Iron is determined in the solution free from **Cu** by adding **Al** strips (or **Zn** if the latter (*i. e.*, **Zn**) is to be determined) in a separate sample to reduce the **Fe** to the ferrous state. The iron content is then determined by  $\text{KMnO}_4$  as on p. 14 ff. A blank must be run on the **Zn** and **Al** used as they both contain **Fe**; done by dissolving 10 grams in  $\text{HCl}$  and either titrating directly or else separating the **Fe** by **Br** and determining the **Fe** by titration or weighing as oxide.

Gold and silver are determined by fire methods. The determination of the lesser constituents is given in Classen and Price and Meade.

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\*  $\text{CuH}_2$ , copper hydrid, is formed momentarily on the cathode during electrolysis.  $\text{HNO}_3$  decomposes (oxidizes) this more readily than  $\text{H}_2\text{SO}_4$ , hence the presence of a little  $\text{HNO}_3$  is necessary in **Cu** analyses. Much  $\text{HNO}_3$  prevents the precipitation of all the **Cu** when much **Fe** is present. See also p. 44, Sand ff.

Some authors suggest the direct electrolysis of a sulfate solution of matte, depending on the slight solubility of  $\text{PbSO}_4$  to give finally all the **Pb** as  $\text{PbO}_2$  on the anode.

## Analysis of

**Sample No.**

[illegible]

**Zn.** Zinc may be determined as follows, using Al to reduce the iron, or using a separate sample.

Boil down the solution containing all some or none of the following (Fe, Al, Mn, Cu) and Zn to 10 cubic centimeters with  $\text{HNO}_3$ , specific gravity, 1.42, add  $\text{KClO}_3$  as above, and evaporate just to dryness. Cool, dissolve in concentrated  $\text{HNO}_3$  and filter off Mn, on asbestos if present. To the filtrate, add 10 grams solid  $\text{NH}_4\text{Cl}$  15 cubic centimeters  $\text{NH}_4\text{OH}$ , and 10 cubic centimeters Br water, boil, filter and wash with warm dilute  $\text{NH}_4\text{Cl}$  solution. Filtrate contains (Cu) and Zn. Rid of the former, if present by passing  $\text{H}_2\text{S}$  to the warm diluted slightly acid solution, or electrolyze. Rid the filtrate of  $\text{H}_2\text{S}$  if used by boiling with  $\text{HCl}$ , and titrate the Zn with  $\text{K}_4\text{Fe}(\text{CN})_6$  solution as on p. 42 or 60.

## Analysis of

**Sample No.**

[illegible]

# ORES.

## COPPER ORES.

There are six methods in use for the determination of Cu in ores; the electrolytic, iodid, sulphocyanid-permanganate, iodate, colorimetric and cyanid arranged in the probable order of greatest accuracy.

The first of these is the most acceptable as it involves only solution and two weighings. It has the disadvantage that it cannot be used with ores containing As, Sb or Bi. They may first be separated, p. 48, and the Cu determined electrolytically.

The iodid is the all-around method. It is not quite as accurate as the electrolytic, and is not used on refined copper or on pure ores in large laboratories.

The sulphocyanid allows of titration with  $\text{KMnO}_4$  but is not as well established as the others. The iodate method is used by a few chemists.

The cyanid method is used for more approximate determinations.

For example, at one of the western plants the electrolytic method is used in the absence of As, Sb, Bi (or Pb). If separations are necessary, the iodid method is employed. For approximate results, the cyanid method is used, or for less than 0.5 per cent. Cu the colorimetric method is used. This last is used chiefly for slags and low-grade ores.

**Procedure No. 19.**—To determine Cu by the iodid method, 1 gram of ore is dissolved in  $\frac{1}{4}$ -liter Erlenmeyer, in  $\text{HNO}_3$ , a few cubic centimeters of HCl added to rid of Ag, and the solution boiled with  $\text{H}_2\text{SO}_4$  to white fumes. Cool, add 30 cubic centimeters water and heat until  $\text{Fe}_2(\text{SO}_4)_3$  dissolves. Precipitate the Cu with either Al or Zn (followed by a little  $\text{H}_2\text{S}$ ) dissolve all the Zn or Al, filter and wash Cu and insoluble on paper. Wash these back into the beaker, using but little water, and dissolve in 10 cubic centimeters  $\text{HNO}_3$  1-2. Boil the solution, pour through the filter, wash with a little Br water to dissolve any CuS caught mechanically, and boil off the Br 5-10 minutes. It has oxidized any As or Sb so that they will not interfere with the titration. Add alkali to first traces of blue color, and distinctly acidify with HAc., forming  $\text{Cu}(\text{Ac})_2$ . To this add 3 grams

## Analysis of

**Sample No.**

[illegible]



KI which has been dissolved in a few cubic centimeters water. This forms  $\text{CuI}$ , liberating one equivalent of iodine for every equivalent of Cu present. This I is titrated at once with 1.96 per cent.  $\text{Na}_2\text{S}_2\text{O}_3$  solution standardized against a known ore, using starch solution, p. 52, as an indicator.

The procedure in the cyanid titration is the same up to the adding of alkali. Faint blue is produced with  $\text{NH}_4\text{OH}$ , and the color almost discharged (giving a pink tint) with ore standardized 2.1 per cent. KCN solution.

A moisture test should be made on the ore in porcelain at  $100^\circ \text{C}$ .

### ZINC IN ORES.<sup>a</sup>

The titration of Zn involves the non-academic procedure of *titrating  $\frac{3}{4}$  of the solution, until the end point is passed; then adding most of the remaining  $\frac{1}{4}$  of the solution titrating to about the end point, and finally rinsing out the auxiliary beaker and getting the true end point.* The indicator ordinarily used is a row of drops of 1 per cent.  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution on a paraffin coated porcelain tile. Breyer has suggested the use of the internal "blue color" in the solution which changes to green at the end point, when  $\text{Fe}^{II}$  is present in the Zn solution and  $\text{Fe}^{III}(\text{CN})_6$  in the ferrocyanid.

The Breyer method given below is for the analysis of complex ores. If Cd is not present, only one  $\text{H}_2\text{S}$  treatment is necessary; if the substance is insoluble e. g., zinc spinel, it must be fused with  $\text{Na}_2\text{CO}_3$  and borax to dissolve it. If pure zinc from brass is to be titrated the requisite amount of  $\text{NH}_4\text{OH}$  and HCl is added to X, p. 62, the 0.4 mg.  $\text{Fe}^{II}$  added and the procedure thence followed:

**Procedure No. 20.**—0.5-1 gram of ore is weighed into a tall covered 250 cubic centimeter Jena beaker, moistened with water and dissolved in 10 cubic centimeters HCl 1.20. Boil the solution, add carefully 10 cubic centimeters  $\text{H}_2\text{SO}_4$  1-1 and boil to fumes. Dilute to 150 cubic centimeters and add 1 gram Al powder. Boil to colorless solution. Filter, pass in  $\text{H}_2\text{S}$ .  $\text{SiO}_2$  and  $\text{H}_2\text{S}$  metals are removed, solution contains Al, Fe, Cd, Zn (Cd is rid of by  $\text{H}_2\text{S}$  or by electrolysis). Procedure; add  $\text{H}_2\text{S}$  to solution, a few drops only of  $\text{NH}_4\text{OH}$  to start precipitates and filter on a paper washed with excess of  $(\text{NH}_4)_2\text{S}_2$ . Rid solution of  $\text{H}_2\text{S}$  by boiling.

## Analysis of

**Sample No.**

[illegible]

Almost neutralize with KOH, finish neutralization with  $\text{Na}_2\text{CO}_3$  (litmus), add a few cubic centimeters  $\text{H}_2\text{SO}_4$  1-5 and precipitate Zn with  $\text{H}_2\text{S}$ . (Zn may be determined from here by roasting and weighing as oxid.) Preferably wash the precipitate on a filter paper, punch a hole in the latter, wash ZnS into a beaker, dissolve in 30 cubic centimeters HCl 1-3, boil off  $\text{H}_2\text{S}$  for 15 minutes, add 13 cubic centimeters  $\text{NH}_4\text{OH}$ , specific gravity 0.90, neutralize this with 3 cubic centimeters HCl 1.20.

X (Brass) dilute to 200 cubic centimeters, and:

Titrate the Zn with 2.2 per cent. "aged"  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  solution as per below. Use either the  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution on tile with the "blue color" check or else the latter only as indicator. Standardize against freshly ignited 0.2-gram ZnO dissolved in 30 cubic centimeters HCl 1-3 + 13 cubic centimeters  $\text{NH}_4\text{OH}$ , specific gravity 0.90, and using the same indicator as for the ore.

Cause of the "blue color" indicator action. If the ferrocyanid solution is allowed to age, gases dissolved in the water will by oxidation cause the formation of  $^{\text{III}}\text{Fe}(\text{CN})_6$ . This latter does not react with Zn, but with the  $\text{Fe}^{\text{II}}$  in the Zn solution. When all Zn is precipitated, the concentration of  $\text{Fe}^{\text{II}} \text{CN}_6$  becomes so great that it causes the decomposition of the blue  $\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$  forming the colorless  $\text{Fe}[\text{Fe}(\text{CN})_6]$ . This color change takes two or three drops at the end point, running from blue through green to colorless. The most satisfactory point to recognize is the change from blue to green. This change comes at about the same place (0.25 cubic centimeter before actually) as the brown color produced on the tile. Hence it may be used to help get the brown color point; or better still, as the actual indicator for both standard and sample.

As directed under brass, it is advisable to experiment with a 1 per cent. solution of  $\text{ZnCl}_2$  until the technique of the divided titration and of the end point is mastered. If the ferrocyanid solution is new, 0.3-gram ferricyanid may be added. If the solution titrated has no Fe, 3-4 milligrams  $\text{Fe}^{\text{II}}$  may be added before titration as directed under brass above. Finally, the same amount of  $\text{NH}_4\text{OH}$  and HCl should be present in all titrations, *viz.*: 10 cubic centimeters HCl, specific gravity 1.20, and 13 cubic centimeters  $\text{NH}_4\text{OH}$ , specific gravity 0.90. This is important.

A moisture test at 100° C. porcelain should be made on the ore.

### LEAD IN ORES.<sup>23</sup>

Pb is most readily determined as  $\text{PbO}_2$ , by the electrolysis of a nitrate solution of the ore, but in the presence of As, Bi, Mn, As (Se, Te,  $\text{P}_2\text{O}_5$ ) the separa-

## Analysis of

**Sample No.**

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tion is incomplete. Therefore Pb is separated by precipitation as  $\text{SO}_4$ , and this precipitate is treated according to the molybdate, bichromate or by electrolysis method. Procedure is to dissolve 1-gram ore in 10 cubic centimeters  $\text{HCl}$  1.2, rid of the latter with 15 cubic centimeters  $\text{HNO}_3$  1.42 by boiling to small bulk. Most of the excess  $\text{HNO}_3$  should be boiled off. If the ore is pure, dilute to 150-200 cubic centimeters and electrolyze. If the ore is not pure, *i.e.*, if it contains one of the above mentioned impurities, Pb should be precipitated as  $\text{PbSO}_4$  after ridding of most of the  $\text{HNO}_3$  neutralizing the remainder, diluting to 50 cubic centimeters 3 grams  $\text{HTr}$  to keep Sb in solution (p. 5), and adding diluted  $\text{H}_2\text{SO}_4$  to it or vice versa (p. 6). Five cubic centimeters  $\text{C}_2\text{H}_5\text{OH}$  should be added to the precipitate and about 10 cubic centimeters added to the wash bottle when washing the  $\text{PbSO}_4$ . The bulk of this should remain in the original beaker. If the  $\text{PbSO}_4$  is to be electrolyzed it is dissolved in hot saturated  $\text{NH}_4\text{NO}_3$  solution, run through the paper onto the precipitate in the beaker, and the solution diluted before adjusting the gauze anode. The electrolysis procedure is the same as under brass and bearing metals.\*

For impure ores the molybdate or the bichromate titration is more often used.

**Procedure No. 21.**—Weigh 0.5-1 gram ore into a  $\frac{1}{4}$ -liter Erlenmeyer, add 10 cubic centimeters concentrated  $\text{HCl}$  and 20 cubic centimeters water, and boil to rid of all  $\text{H}_2\text{S}$ . Any insoluble residue other than  $\text{SiO}_2$  is dissolved by the addition of 10 cubic centimeters  $\text{HNO}_3$  and 7 cubic centimeters  $\text{H}_2\text{SO}_4$  added to precipitate the  $\text{PbSO}_4$ . Boil to white fumes to rid of  $\text{HNO}_3$ , stand to cool, dilute to 50 cubic centimeters and allow to stand until the  $\text{Fe}_2(\text{SO}_4)_3$  dissolves. Cool filter, and wash, adding a few cubic centimeters  $\text{H}_2\text{SO}_4$  to the wash bottle.

Transfer paper with precipitate to original flask. Disintegrate the paper by boiling with 10 cubic centimeters  $\text{HCl}$  1.20 total bulk about 70 cubic centimeters. Add 15 cubic centimeters more  $\text{HCl}$ , cool, add a little water if too dilute, and

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\* The precipitation of  $\text{PbO}_2$  from pure solution is aided by the addition of a small amount of  $\text{Cu}(\text{NO}_3)_2$  solution.  $\text{Cu}^{++}$  discharges more readily than  $\text{H}^+$ , hence the opposite ion  $\text{PbO}_2^-$  — will thus more readily precipitate.

## Analysis of

**Sample No.**

[illegible]

make distinctly alkaline with  $\text{NH}_4\text{OH}$ . Make distinctly acid with glacial  $\text{HAc}$ . Heat to dissolve completely the  $\text{PbSO}_4$ , and dilute to 200 cubic centimeters with boiling water.

Divide the solution into two parts and titrate hot with 0.425 per cent.  $(\text{NH}_4)_2\text{MoO}_4$  solution. The indicator used is 0.5 per cent. tannin solution dropped onto the tile. A yellow color develops at the end point. The same divided titration is used as with  $\text{Zn}$ ; and it is advisable to study this, using a 0.15 per cent. solution of  $\text{Pb}(\text{NO}_3)_2$  before attempting the actual titrations. The molybdate solution is standardized against 0.2230-gram  $\text{PbSO}_4$  treated as the ore beginning with the litmus and  $\text{NH}_4\text{OH}$  treatment.

A moisture test in porcelain at  $100^\circ\text{C}$ . should be run on the ore.

### **$\text{Al}_2\text{O}_3$ IN BAUXITE.**

**Procedure No. 22.**—Fuse 5 grams of pulverized sample with  $\text{Na}_2\text{O}_2$ , dissolve the melt in  $\text{H}_2\text{O}$  and re-fuse the insoluble in  $\text{Na}_2\text{O}_2$ , dissolve again and make up the combined filtered filtrates to 1 liter. Acidify an aliquot part usually 1/10 with  $\text{HNO}_3$ , add a slight excess,  $\text{NH}_4\text{OH}$ , redissolve, reprecipitate. Filter, ignite in  $\text{Pt}$ , treat with  $\text{H}_2\text{F}_2 + \text{H}_2\text{SO}_4$ , ignite on the ring burner and weigh as  $\text{Al}_2\text{O}_3$ , 53.03 per cent.  $\text{Al}$ .

A moisture test is advisable.

## Analysis of

**Sample No.**

[illegible]





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